NASA CONTRACTOR REPORT 166487

(NASA-CR-166487) SYNTHESIS, CHARACTERIZATION AND POLYMERIZATION OF FLUOROCARBON ETHER ELASTOMERS Final Report, 1 Oct. 1980 - 10 Dec. 1982 (San Jose State Univ., Calif.) 48 p HC A03/MF A01 CSCL 11G G3/23 N83-31723 Unclas 13414

Synthesis, Characterization and Polymerization of Fluorocarbon Ether Elastomers

T. S. Chen
C. H. Cheng
M. Taylor

NASA Co-operative
Agreement No. NCC2-81

NASA

NASA CONTRACTOR REPORT 166487

Synthesis, Characterization and Polymerization of Fluorocarbon Ether Elastomers

Timothy S. Chen
C. H. Cheng
M. Taylor
San Jose State University
San Jose, California 95192

Prepared for
Ames Research Center
under NASA Co-operative
Agreement No. NCC2-81

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

Forword

This report descrobes the work performed by San Jose State University Foundation under NASA Co-operative Agreement No. NCC 2-81, "Synthesis, Characterization and Polymerization of Fluorocarbon Ether Elastomers." The investigations were carried out during the period from October 1, 1980 to December 10, 1982 by Dr. C. H. Cheng, Mr. M. Taylor and Dr. Timothy S. Chen, principal investigator. This co-operative agreement was administered by NASA Ames Research Center with Dr. Robert W. Rosser as project monitor.

TABLE OF CONTENTS

Perfluoroalkyleneether Triazine Elastomers(1)

Introduction

Efforts to synthesize high-temperature elastomers for use in extreme environments have been continuing over the past decade. Model studies utilizing heterocyclic rings with fluoroalkylether and fluoroalkylether substituents have clearly shown that properly substituted 1,2,4 oxadiazole and 1,3,5 triazine rings when organized into a polymeric system should lead to thermally, oxidatively and hydrolytically stable elastomers (1,2). Initial attempts to synthesize polymers having an adequate molecular weight between crosslinks were coupled by a high sensitivity toward reaction conditions.

Recently, we have shown that perfluoroalkylether oxadiazole elastomers exhibit good thermal, oxidative and hydrolytic stability as well as low-temperature flexibility (3,4). A method was also found to synthesize perfluoroalkylether triazine elastomers having slightly better thermal properties than the oxadiazole ; however, the reaction sequence for making the triazine was not entirely satisfactory as the pre-polymer chain-length was difficult to control and reproduce.[5] Moreover, the resulting polymer manifested hydrolytic instability due to the particular agent utilized in the ring-closing step.

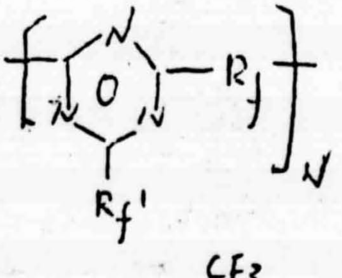
In this article, we wish to report an improved procedure for making perfluoroalkylether-triazine elastomers, and, more specifically, the synthesis of 2,4-perfluoroalkylenether-6-perfluoroalkylether triazine having the following repeating unit:

"2,4,6-Perfluoroalkylether Triazine Elastomers"

The stringent requirements of fuel-tank sealants for future supersonic aircraft has been stimulating the search for the past decade. Perfluoroalkylether oxadiazole elastomers (1-2) have been synthesized and exhibit good thermal, oxidative, hydrolytic stability, low glass transition temperatures, and chemical inertness. However, attempts to increase the chain length between two crosslinks for good physical and mechanical properties have been crippled by the high sensitivity toward reaction conditions. Recently the relatively high molecular weight perfluoroalkylether oxadiazole elastomers have been obtained (3,4) and gave good thermal, oxidative, hydrolytic stability as well as low temperature flexibility.

Another thermal stable 2,6-perfluoroalkylether 4 trifluoromethyl triazine elastomers were synthesized (5) and differed from perfluoroalkylether oxadiazole elastomers by using triazine ring as chain-extension linkage instead of oxadiazole ring. The result gave somewhat better physical and thermal properties; however, it resulted in a hydrolytically unstable elastomer due to the particular ring closing agent. Moreover, it was very difficult to control the prepolymer chain-length, due to a process which exhibited reproducibility problems.

In this article we wish to report the synthesis of 2,4,6-Perfluoroalkylether triazine elastomers with the following repeating unit



where:

$$R_f = -\!\left[\overset{CF_3}{\overset{|}{C}}F-(OCF_2\overset{CF_3}{\overset{|}{C}}F)_m O-(CF_2)_5 O-(\overset{CF_3}{\overset{|}{C}}F-CF_2O)_n\overset{CF_3}{\overset{|}{C}}F\right]\!-$$

$$R_f' = -\overset{CF_3}{\overset{|}{C}}F\left(OCF_2-\overset{CF_3}{\overset{|}{C}}F\right)_p F$$

$$N = 2-8$$

This new method gives elastomers with high thermal and oxidative we have achieved a better procedure properties and with the use of a branched ring closing reagent a much improved hydrolytic stability. In addition we are able to obtain reproducible and consistent physical and mechanical property. While retaining a glass transition temperature (Tg) of 45°C. Thus, this process provides a way to control molecular weights according to the particular physical properties desired.

Experimental

All Infrared (IR) spectra were recorded on a Nicolet MX-1 FT-IR Spectrometer. Thermogravimetry measurements were recorded with the DuPont Instruments, 951 thermogravimetry analyzer and 990 thermal analyzer. Glass transition temperatures (Tg) were obtained with a DuPont differential scanning calorimetry (DSC) cell and 1090 thermal analyzer. All gel permeation chromatography measurements were done with a Waters Associates ALC-GPC 202/401 liquid chromatograph equipped with Spectra-Physics SP 4020 data interface, SP 4000 center processer unit and SP 4000 printer and plotter. The S-P system was programmed to correct for baseline and to compute the average molecular weight by imputting known calibration points. Separations were obtained by using DuPont size exclusion (SE) columns and detected by Waters Associates differential UV dectector at 254 mm or differential refractometer R 401 in Freon 113 solution (7). Gas chromatography results were obtained with a Hewlett-Packard Model 5830 gas chromatograph.

1,1,2-Trichloro-1,2,2-trifluoro ether (Freon 113) was purchased from Fischer Scientific Company and distilled from a 4 ft column of Fischer Scientific 6 mm porcelain berl saddles at 48°C. Perfluoroalkylether diacide fluorides (EDAF) were purchased from PCR Inc., and Technochemie (GMBH, West Germany). Hexafluoropropyl epoxide was obtained from DuPont de Nemours and Co. without further purification. Other chemicals were either analytical grade or better.

Preparation of perfluoroalkylether acid fluoride ($R_f C^{=0}-F$)

To a 1000 ml two-neck flask was added 10 gm of sodium floride, 10 gm of cesium fluoride (both were dried at 200°C overnight) and 20 ml of tetraglyine (Bis (2-(2-methoxy-ethoxy ethyl)ether). Then hexafluoropropylene epoxide was condensed (2-3 ml/min) into the flask with vigorous stirring. After 10-20 min induction time the solution became slightly exothermic indicating that the reaction had been initiated. Addition of liquid hexafluoropropylene epoxide was continued until the flask was filled to 2/3 of its capacity. The solution distillation of yielded three fractions which were collected and identified by gas chromatography in Table 1.

Analytical data: IR (film)

1880, 1870 cm^{-1} ($-C^{=0}$)

1400-1050 cm^{-1} (C-F)

Preparation of perfluoroalkylether acid ($R_f COOH$)

To 50 gm of perfluoroalkylether acid fluoride was added 10 ml of H=0. The mixture was then stirred for one hr. Excess H_2O was removed by drying at 120°C under vacuum overnight. 47 gm of perfluoroalkylether acid was obtained.

Analytical data: IR (film)

1780 cm^{-1} (-C=o) 1400-1050 cm^{-1} (C-F)

3300-2900 cm^{-1} (OH)

Preparation of perfluoroalkylether acid anhydride

To 200 gm of perfluoroalkylether acid was added 160 gm of phosphorous pentaoxide (P_2O_5). The mixture was heated at 180°C for at least 16 hrs. and then vacuum distilled. 150 gm of perfluoroalkylether acid anhydride was collected (85°C/16 mm Hg - 120°C/0.5 mm Hg).

Analytical data: IR (film)

1825, 1815 cm^{-1} (C=0)

1400-1050 cm^{-1} (C-F)

ORIGINAL PAGE IS
OF POOR QUALITY

Preparation of perfluoroalkylether diamide (R_f-$(CONH_2)_2$)

To 200 gm of perfluoroalkylether diacid fluoride was added 150 ml of Freon 113. Ammonia was then condensed into the solution with vigorous stirring. The reaction was exothermic and completed after the temperature of the solution cooled down by excess liquid. The NH_3 solution was then filtered to remove the ammonium fluoride and Freon 113 was then removed on a rotary evaporator. 190 gm of perfluoroalkyl ether diamide was collected without further purification.

Analytical data: IR (film) 3500 cm^{-1}, 3140-3450cm^{-1} (N-H)

1730-1750, 1600cm^{-1} (C=O) 1400-1050cm^{-1} (C-F)

Preparation of perfluoroalkylether dinitrile (NC-R_f-CN)

To 200 gm of perfluoroalkylether diamide in a 500 ml round bottom flask was added 200 gm of phosphorus pentaoxide (P_2O_5). The mixture then was mixed thoroughly and then heated at 200°C for at least 24 hrs. Perfluoroalkylether dinitrile was vacuum distilled and two fractions were collected. The first fraction was collected at 25°C at 760 mm Hg to 80°C at 20 mm Hg (30 gm) and the second fraction was collected from 80°C at 20 mm Hg to 130°C at 0.5 mm Hg (140g). Gas chromatography indicated that the lower boiling materials contained molecular weight fractions corresponding to M+M<2 and the higher boiling materials contained fractions corresponding to M+M 3 to 8. (Table II)

Analytical data: IR (film) 2260cm^{-1} (-C≡N)

1400-1050 cm^{-1} (C-F)

Preparation of perfluoroalkylether diamidine (H_2NNH C R_f - CNH NH_2)

20 ml of NH_3 was condensed into a 100 ml three neck flask equipped with a dry-ice condenser, an NH_3 gas inlet, and an addition funnel. A solution of 10 gm perfluoroalkylether dinitrile in 10 ml of Freon 113 was added dropwise into the flask with vigorous stirring. After completion of the addition, excess ammonia and Freon 113 were removed under vacuum. Perfluoroalkylether diamidine (10.5 gm) then

was collected without farther purification.

Analytical data IR (film) : 3200-3000 cm^{-1} (NH).
1684 cm^{-1} (C=N) 1100-1050 cm^{-1} (C-F)

Preparation of perfluoroalkylether (imidoylamidine) dinitrile (I)

$$NC-R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}-R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}-R_f-CN$$

(I)

To a solution of 20 gm perfluoroalkylether dinitrile in 20 ml Freon 113 was added dropwise the solution of 10 gm perfluoroalkylether diamidine in 10 ml Freon 113 with vigorous stirring for 2 hrs. After evaporating the solvent, 30 gm of perfluoroalkylether (imidoylamidine) dinitrile (I) was recovered.

GPC: $M_{avg} = 3500$

Analytical data: IR (film) 3500, 3440, 3120 cm^{-1} (N-H), 2260 (-C≡N)
1652, 1602, 1520 cm^{-1} ($-\overset{N}{\overset{\|}{C}}=N-\overset{N}{\overset{\|}{C}}-$) 1400-1050 cm^{-1} (C-F)

Preparation of perfluoroalkylether (imidoylamidine) diamidine (II)

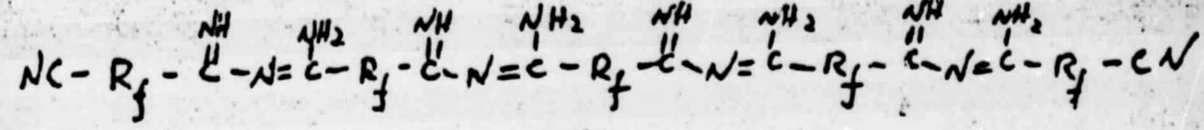
$$\overset{HN}{\underset{H_2N}{\diagup}}C-R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}-R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}-R_f-\overset{NH}{\overset{\|}{C}}-NH_2$$

(II)

To 30 ml of liquid ammonia was added dropwise perfluoroalkylether (imidoylamidine) dinitrile (I) (30 gm in 30 ml Freon 113). With vigorous stirring for 3 hrs. Excess ammonia and solvent were then removed under vacuum and 30 gm of perfluoroalkylet (imidoylamidine) diamidine (II) was obtained without further purification.

Analytical data: IR (film) 3600-3000 cm^{-1} (NH) 1684 cm^{-1} (C=N), 1652, 1602, 1520 cm^{-1}, ($-\overset{N}{\overset{\|}{C}}-N=\overset{N}{\overset{|}{C}}-$), 1400-1050 cm^{-1} (C-F)

Preparation of perfluoroalkylether (imidoylamidine) dinitrile (III)



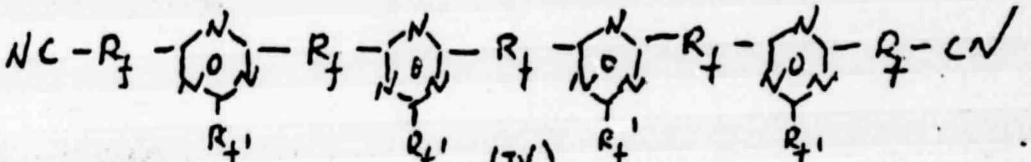
(III)

30 gm of perfluoroalkylether (imidoylamidine) diamidine in 30 ml Freon 113 was added dropwise into a solution of 20 gm perfluoroalkylether dinitrile in 20 ml Freon 113 with vigorous stirring for 4 hrs. After removing the solvent under vacuum 50 gm of perfluoroalkylether (imidoylamidine) dinitrile (III) was recovered.

Analytical data: IR (film) 3600-3000 cm^{-1} (N-H).

2260 cm^{-1} (-C≡N) 1650, 1602, 1520 cm^{-1} (-C(=N)-N=C(-N)-) 1400-1050 cm^{-1} (C-F)

Preparation of perfluoroalkylether (triazine) dinitrile (IV)



(IV)

To 100 gm of perfluoroalkylether acid anhydride was added 25 gm of perfluoroalkylether (imidoylamidine)-dinitrile (III) in 30 ml Freon 113 with vigorous stirring for 2 hrs. After removing the solvent under vacuum, the side product, perfluoroalkylether acid, and excess perfluoroalkylether acid anhydride were pumped out by vacuum distillation. 35 gm of perfluoroalkylether (triazine) dinitrile (IV) was obtained.

Analytical data: IR (film) 2260 cm^{-1} (-C≡N)
1550 cm^{-1} (triazine)
1400-1050 cm^{-1} (C-F)

G.P.C : M_w = 6200

Preparation of high performance perfluoroalkylether triazine elastomers

35 gm of perfluoroalkylether(triazine)dinitrile (IV) was treated with liquid ammonia and then heated in an oven at 150°C for 4 days. The resulting product (35gm) was a light tan perfluoroalkylether triazine elastomer with excellent properties.

Analytic data: IR (film) 1550 cm^{-1} (Triazine)
1400-1050 cm^{-1} (C-F)

Results and Discussions

Perfluoroalkylether dinitrile reacts with ammonia rapidly to form the corresponding diamidine.

$$NC\text{-}R_f\text{-}CN + NH_3(l)\ \text{(excess)} \longrightarrow H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}R_f\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH_2 \quad \cdots (1)$$

Reaction (1) was instantaneous and gave near 100% yield. The addition of perfluoroalkylether diamidine to perfluoroalkylether dinitrile produced perfluoroalkylether(imidoylamidine)dinitrile (I).

$$H_2N\text{-}\overset{\overset{HN}{\|}}{C}\text{-}R_f\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH_2 + NC\text{-}R_f\text{-}CN \longrightarrow NC\text{-}R_f\text{-}\overset{\overset{NH}{\|}}{C}\text{-}N{=}\overset{\overset{NH_2}{|}}{C}\text{-}R_f\text{-}\overset{\overset{NH}{\|}}{C}\text{-}N{=}\overset{\overset{NH_2}{|}}{C}\text{-}R_f\text{-}CN \quad \cdots (2)$$

(I)

The formation of imidoylamidine semiring was indicated by IR bands at 1520 cm^{-1}, 1600 cm^{-1} and 1650 cm^{-1}. The yield of reaction (2) determined by molecular weight distribution measurements (GPC) was ~70%

In order to control molecular weight distribution, it is very critical to have excess liquid ammonia in Reaction (1). According to Reaction (2) any unreacted perfluoroalkylether dinitrile would react with perfluoroalkylether diamidine to form the imidoylamidine linkage that would broaden the molecular weight distribution thereafter. Also the order of addition is also very important in controling molecular weight distribution. Any orders differ from the previously described would result in broadening molecular weight distribution.

Perfluoroalkylether(imidoylamidine)dinitrile (I) was added into excess liquid ammonia to give perfluoroalkylether(imidoylamidine)diamidine (II)

$$NC\{R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}-\}_2R_f-CN + NH_3(l) \longrightarrow H_2N\overset{NH}{\overset{\|}{C}}\{R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}\}_2R_f-\overset{NH}{\overset{\|}{C}}-NH_2 \qquad (3)$$

(II)

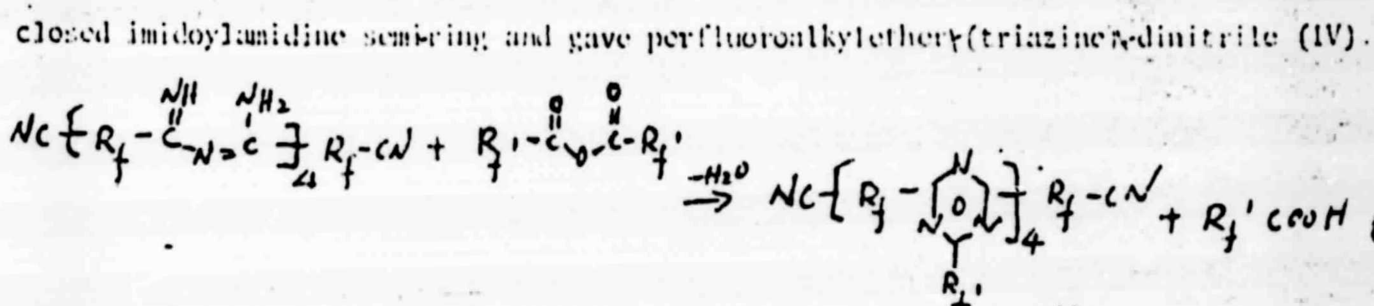
Repeated reaction (2) by using perfluoroethers(imidoylamidine)diamidine (II) instead of perfluoroalkylether diamidine, the perfluoroalkylether(imidoylamidine)-dinitrile (III) was obtained. The molecular weight distribution curve (GPC)

$$NC\{R_f-\overset{NH}{\overset{\|}{C}}-N=\overset{NH_2}{\overset{|}{C}}\}_4R_f-CN$$

(III)

indicated that ~63% of the molecules reached the length of compound III. Table (III) Theoretically by using this stepwise method, one should be able to build-up molecular weight as large as one wished. However the longer the chain is, the slower the reaction rate will be, and the lesser molecules will reach the desired length.

The addition of compound (III) into excess perfluoroalkylether acid anhydride closed imidoylamidine semi-ring and gave perfluoroalkylether(triazine)-dinitrile (IV).

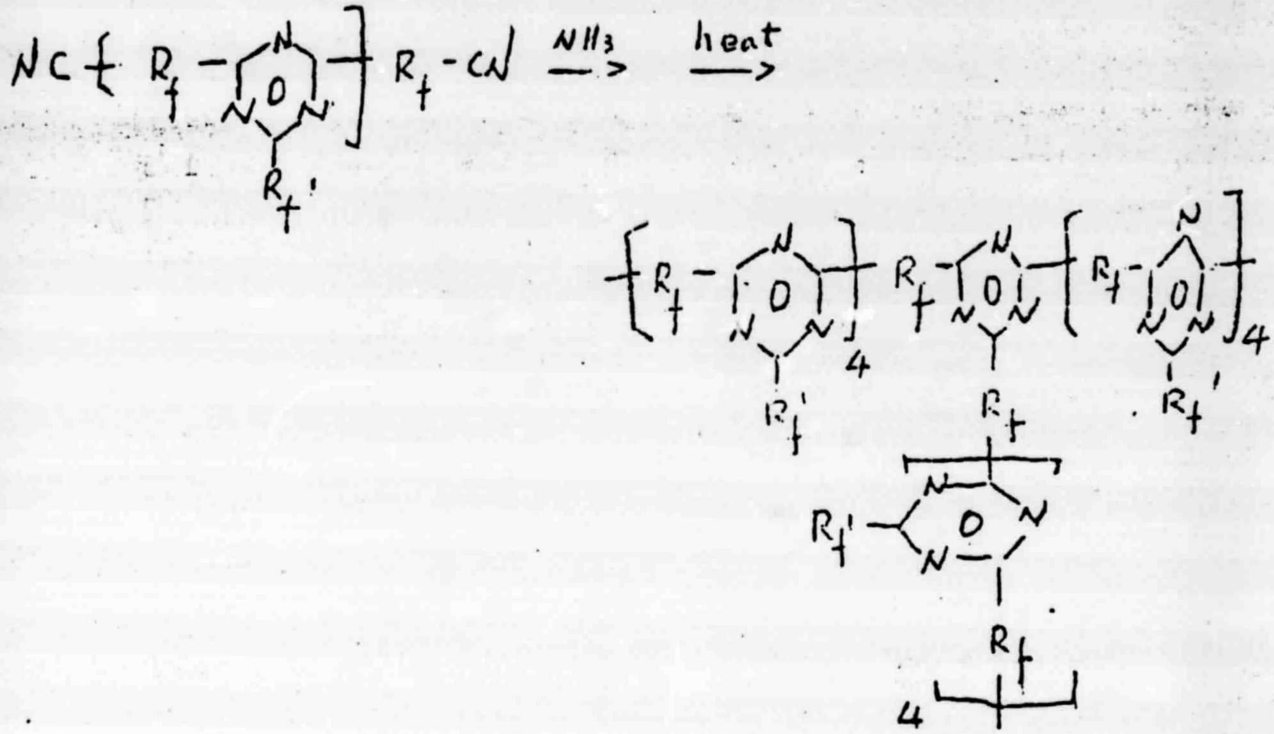
 (4

(IV)

The use of excess acid anhydride served as the drying agent to remove water produced in this ring-closing reaction.

This stepwise chain build-up method allows one to control molecular weight and its distribution from the GPC molecular weight distribution measurement a yield of ~60% was obtained for compound (IV) from starting materials.

Linear prepolymer (IV) was converted into amidine form and heated at 150°C oven for four days. The light tan thermally stable perfluoroalkylether triazine elastomer were obtained with the proposed structure of compound (V).



(V)

The cured perfluoroalkylether triazine elastomer had a glass transition temperature (Tg) of -45°C, and was hydrolytical stable in boiling water for two weeks without any weight loss or property deterioration. Isothermal weight losses of this material were measured and are listed in Table (IV) together with 1,5-perfluoroalkylether 3 trifluoror triazine elastomer and poly (trifluoropropylmethyl siloxane) for comparison. Isothermal weight losses of this ~~high performance~~ 1,3,5-perfluoroalkylene ether triazine elastomer both in nitrogen and air were much lower than 1,5-perfluoroalkylether 3 trifluoromethyl triazine elastomers, perfluoroalkylether oxadiazole elastomers [illegible]

ORIGINAL PAGE IS
OF POOR QUALITY

In conclusion, this stepwise synthesis method lays a way which allows one not only to extend the chain-length of perfluoroalkylether polymers but also to control the molecules weight and its distribution. By this method 1,3,5 perfluoroalkylether triazine elastomers was synthesized and it offers excellent oxidative and thermal stabilities which provide itself as a potential candidate for future high temperature applications.

ORIGINAL PAGE IS OF POOR QUALITY

References

1. K. J. L. Paciorek, R. H. Kratzer, J. Kaufman and R. W. Rosser, J. Fluorine Chem., 6, 241 (1975)

2. K. J. L. Paciorek, R. H. Kratzer, J. Kaufman, J. H. Nakahara, R. W. Rosser and J. A. Parker, J. Fluorine Chem., 10, 119 (1977)

3. R. W. Rosser, R. A. Korus, I. M. Shalhoub and H. Kwong, J. of Polymer Science, Polymer Letters Ed., 17, 635 (1979)

4. R. W. Rosser, C. H. Cheng and T. S. Chen (unpublished results)

5. R. W. Rosser and R. A. Korus, J. of Polymer Science, Polymer Letters Ed., 18, 135 (1980)

6. R. A. Korus and R. W. Rosser, Anal. Chem., 50, 249 (1978)

Table I. Molecular Weight Distribution of Perfluoroalkylether Acid Fluoride (G C)

$$F\{C(CF_3)-CF_2-O\}_p\,C(F_3)-C(O)F$$

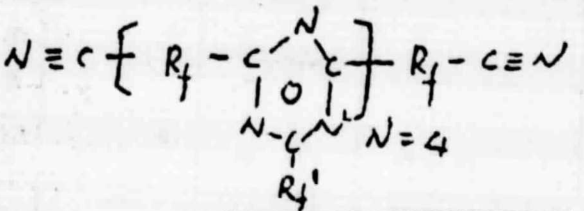
P	%	Boiling Pt
1	60	58°C at 760 mm Hg
2	30	115°C at 760 mm Hg
3 - 5	10	70°C at 0.6 mm Hg

Table II. Molecular Weight Distribution of Perfluoroalkylether dinitrile (GC)

$$N\equiv C\left\{\overset{CF_3}{\overset{|}{C}F}(OCF_2\overset{CF_3}{\overset{|}{C}F})_m O(CF_2)_5 O(\overset{CF_3}{\overset{|}{C}F}-CF_2O)_n\overset{CF_3}{\overset{|}{C}F}\right\}C\equiv N$$

M + N	%
3	1.4
4	5.3
5	33.3
6	41.8
7	15.7
8	2.5

Table III Molecular Weight Distribution of 1.3.5-Perfluoroalkyl ether triazine d.n.



N	%
4	56
3	15
2	18
0	11

Table IV Comparison of Isothermal Weight Loss

Atmosphere	Temperature (°C)	Time (hr)	Weight Loss: 1, 3, 5 perfluoroalkylether triazine elastomers	Weight Loss: Perfluoroalkylether* triazine elastomers	Weight Loss: Poly (trifluoropropylmethyl Siloxane) Elastomers
N_2	300	10	1.0	2.1	9.5
		65	4.3	6.5	17.5
		72	5.5	—	—
N_2	325	10	1.5	3.7	11.8
		48	6.5	—	—
		65	—	9.6	19.2
AIR	300	4	0.3	0.8	42.5
		8	0.8	1.5	75.7
		16	2.1	2.3	77.0
		65	7.5	—	—
		90	10.6	—	—
AIR	325	4	0.8	8.5	73.5
		8	2.0	12.5	76.2
		16	4.5	17.5	77.5
		48	11.5	—	—

ORIGINAL PAGE IS OF POOR QUALITY

* Data from Reference (5)

Perfluoroalkyleneether Triazine Elastomers(II)

The search for the high performance furl-tank sealents in the past decade has resulted in excellent elastomers based on fluorocarbon ether[1,2]. In our earlier paper[3], we reported that an improved perfluoroalkyleneether triazine elastomer was synthesized stepwise and exhibited high thermal and hydrolytic stability, and oxidative and chemical resistance. It also provided a way to control molecular weight according to the particular physical properties desired. However it was later experienced that with the stepwise synthesis method, the higher the molecular weight goes, the lower the yield turns out. To encounter this difficulty, perfluoroalkyleneether dinitrile(EDAF-dinitrile) was first converted into perfluoroalkyleneether diamidine(EDAF-diamidine). EDAF-diamidine then reacted with EDAF-dinitrile in Freon 113 solution to give linear poly(EDAF-imidoylamidine). By controling the molar ratio of EDAF-diamidine to EDAF-dinitrile, the relatively high molecular weight poly(EDAF-imidoylamidine) can readily be obtained, and the thermally cured perfluoroalkyleneether triazine elastomer showed better physical and mechanical properties. A similar method has been applied to obtained high molecular weight perfluoroalkyltriazine elastomers[4,5].

EXPERIMENTAL

1,1,2-Trichloro-1,2,2-trifluoroethan(Freon 113) purchased from Fisher Scientific Co. was distilled prior to use. Perfluoroalkylether diacid fluorides(EDAF) FOC-R_f-COF, where R_f is

$$-\overset{CF_3}{\overset{|}{C}}F\left(OCF_2\overset{CF_3}{\overset{|}{C}}F\right)_m O\left(CF_2\right)_5 O\left(\overset{CF_3}{\overset{|}{C}}FCF_2O\right)_n\overset{CF_3}{\overset{|}{C}}F-$$

and m+n = 6 to 8, were purchased from Technochemie GmbH - Verfahrenstechnik. Perfluoroalkylether dinitrile(EDAF-dintrile) and perfluoroalkylether acid anhydride were prepared as described in our earlier papers.[1,3]

Infrared(IR) spectra were recorded on the Nicolet MX-1 FT IR Spectrophotometer. Viscosities were measured by using a Cannon-Ubbelohde viscometer(size 50) at 25°C.

Perfluoroalkylene-ether Triazine Elastomer Synthesis

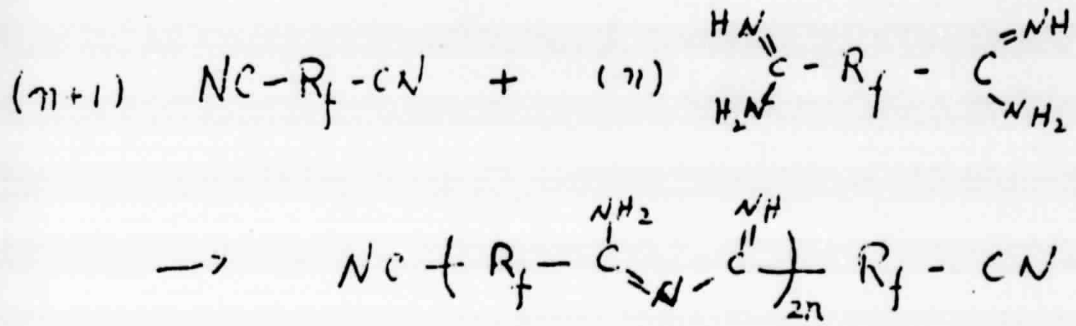
Ammonia was condensed into a tree-neck flask containing 20 ml Freon 113, and equipped with a dry-ice condenser, a gas inlet and an addition funnel. The mixture was stirred for 30 min. The excess ammonia and solvent were then removed and a viscous product which was identified by IR as perfluoroalkylene-ether diamidine(EDAF-diamidine) (10g) was obtained.

In a typical polymerization of the EDAF-dinitrile and EDAF-diamidine, 2.5g of EDAF-dinitrile was added into 2.5g of EDAF-diamidine in 5 ml of Freon 113. The reaction vessel was immersed in a 50°C oil bath. IR and viscometer was used to monitor the degree of polymerization. The reaction was complete when the viscosity of the reaction solution reached a plateau. Ring closure of the resulting polyperfluoroalkylene-ether-(iminoylamidine)dinitrile was done by following the method described earlier(3), a clean viscous liquid was then obtained and indentified as polyperfluoroalkylene-ether(triazine)dinitrile. Ammonia saturated polyperfluoroalkylene-ether(triazine)dinitrile was heated in an oven at 150°C for 3 days. The cured product was a light tan perfluoroalkylene-ether triazine elastomer with excellent properties.

ORIGINAL PAGE IS
OF POOR QUALITY

RESULTS AND DISCUSSION

Solution polymerization of perfluoroalkylene-ether dinitriles (EDAF-dinitrile) and EDAF-diamidines in Freon 113 solvent gives polyperfluoroalkylene-ether-(imidoylamidine)dinitriles. By reacting (n+1) moles of EDAF-dinitrile with (n) moles of EDAF-diamidine, polyperfluoroalkylene-ether(imidoylamidine)-with nitrile (-C≡N) terminal groups was obtained.(Scheme I).



SCHEME(I)

The degree of polymerization of this reaction was monitored by IR spectroscopy and viscosity measurements. Nitriles groups (-C≡N) gave an IR band at 2260 cm^{-1} while imidoylamidine (-C-N=C-) showed three bands at 1520, 1600, and 1650 cm^{-1}. The ratio of IR absorbance at 1600 cm^{-1} and 2260 cm^{-1} was used to estimate the degree of polymerization.(Figure 1). In general, the polymerization was complete after the viscosity of the reaction solution reached a plateau. By varying (n) in Scheme (I), a wide range of different molecular weight polyperfluoroalkylene-ether(imidoylamidine)dinitriles were prepared.

The solution polymerization of EDAF-dinitriles and EDAF-diamidine is a slow process at room temperature and it needs several days to complete at

ORIGINAL PAGE IS
OF POOR QUALITY

At higher temperatures the reaction is faster, however, crosslinking reaction could interfere and reduce the polymer chain length.. The polymerization is best carried out at temperature around 50°C. Under optimum conditions described in the experimental section, A polyperfluoroalkylene-ether(imidoylamidine)dinitrile with molecular weight around 15,000 was prepared without any difficulty.(Table I). The addition of polyperfluoroalkylene-ether(imidoylamidine)dinitrile into perfluoroalkyl acid angydride produced polyperfluoroalkylene-ether-

(triazine)dinitrile. The resulting polyperfluroroalkylene-ether(triazine)-dinitrile was then converted to the corresponding diamidine with ammonia and heated at 150°C for three days to give perfluoroalkylene-ether triazine-elastomer. Table(II) illustrats the physical properties of two perfluoro-alkylene-ether triazine elastomers with different prepolymers. It is concluded that the thermal stability and mechanical properties may be improved by increasing the chain length of the prepolymers. Figure (II) shows the thermograms of perfluoroalkylene-ether triazine - elastomers in both nitrogen and air. The elastomer was thermally and oxidatively stable up to 300°C. Table (III) illustrates the stabilities of perfluoro-alkylene-ether triazine elastomers in boiling water and 50% H_2SO_4 solution. It exhibits an excellent stability in both boiling water and 50% H_2SO_4 solution.

ORIGINAL PAGE IS
OF POOR QUALITY

In conclusion, it is demonstrated that a modified synthesis method has been achieved to overcome the yield problem of the stepwise synthesis method. It also provides a better way to synthesis high molecular weight perfluoroalkylene-ether triazine elastomers. The physical and mechanical properties of the elastomers synthesized by the modified method were better compared with that achived in our earlier papers.

ORIGINAL PAGE IS
OF POOR QUALITY

REFERENCES

1. R. W. Rosser, R. A. Korus, I. M. Shalhoub, and H. Kwong, J. of Polymer Science, Polymer Letters Ed., V17, 635(1979)

2. R. W. Rosser, R. A. Korus, J. of Polymer Science, Polymer Letters Ed., V18, 135(1980).

3. R. W. Rosser, T. S. Chen, and C. H. Cheng, J. of Polymer Science, Polymer Letters Ed., V20, 467(1982).

4. E. Dorfman, W. E. Emerson, R. L. K. Carr, and C. T. Bean, Rubber Chem. Technol., 39(4), 1175(1966).

5. H. C. Brown, P. D. Shuman, and J. Turnbull, J. of Org. Chem., 32, 231(1967).

6. R. A. Korus and R. W. Rosser, Anal. Chem., 50, 249(1978)

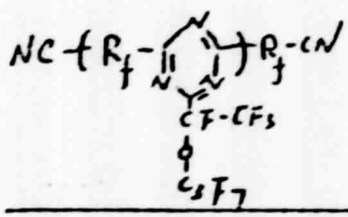
TABLE (I) PREPARATIONS OF POLY(INIDOULAMIDINE)DINITRILES AND THEIR MOLECULAR WEIGHTS

RUN	REACTION TIME(HR)	REACTION TEMP(^{o}C)	(η) (dl/g)	M_v[1]
1	20	50	7.8	14,600
2	20	50	7.7	14,200

(1) Viscosity average molecular weight was calculated from the equation. $M_v = \left(\frac{(\eta)}{k}\right)^{1/a}$

where $k = 4.0 \times 10^{-3}$, $a = 0.55$. (6)

TABLE (II) PHYSICAL PROPERTIES OF CURED PERFLUOROALKYLENE-ETHER TRIAZINE ELASTOMERS

PREPOLYMER	M_w	CURED ELASTOMER(1)	T_g(^oC)	T_d(^oC)(2)
$NC-R_f-CN$	~ 1600	BRITTLE	-30	390
	~15,000	ELASTIC	-45	470

(1) Cured with NH_3 at 150 ^oC.

(2) Decomposition temperature of 5% weight loss in N_2 at a heating rate of 10 ^oC/min.

TABLE (III) STABILITY AND CHEMICAL RESISTANCE OF PERFLUOROALKYLENE-ETHER-TRIAZINE ELASTOMER

REAGENT	TEMPERATURE (°C)	OBSERVATION
H_2O	100	NO PROPERTY CHANGE UP TO TWO WEEKS
50% H_2SO_4	80	NO PROPERTY CHANGE UP TO ONE WEEK

ORIGINAL PAGE IS
OF POOR QUALITY

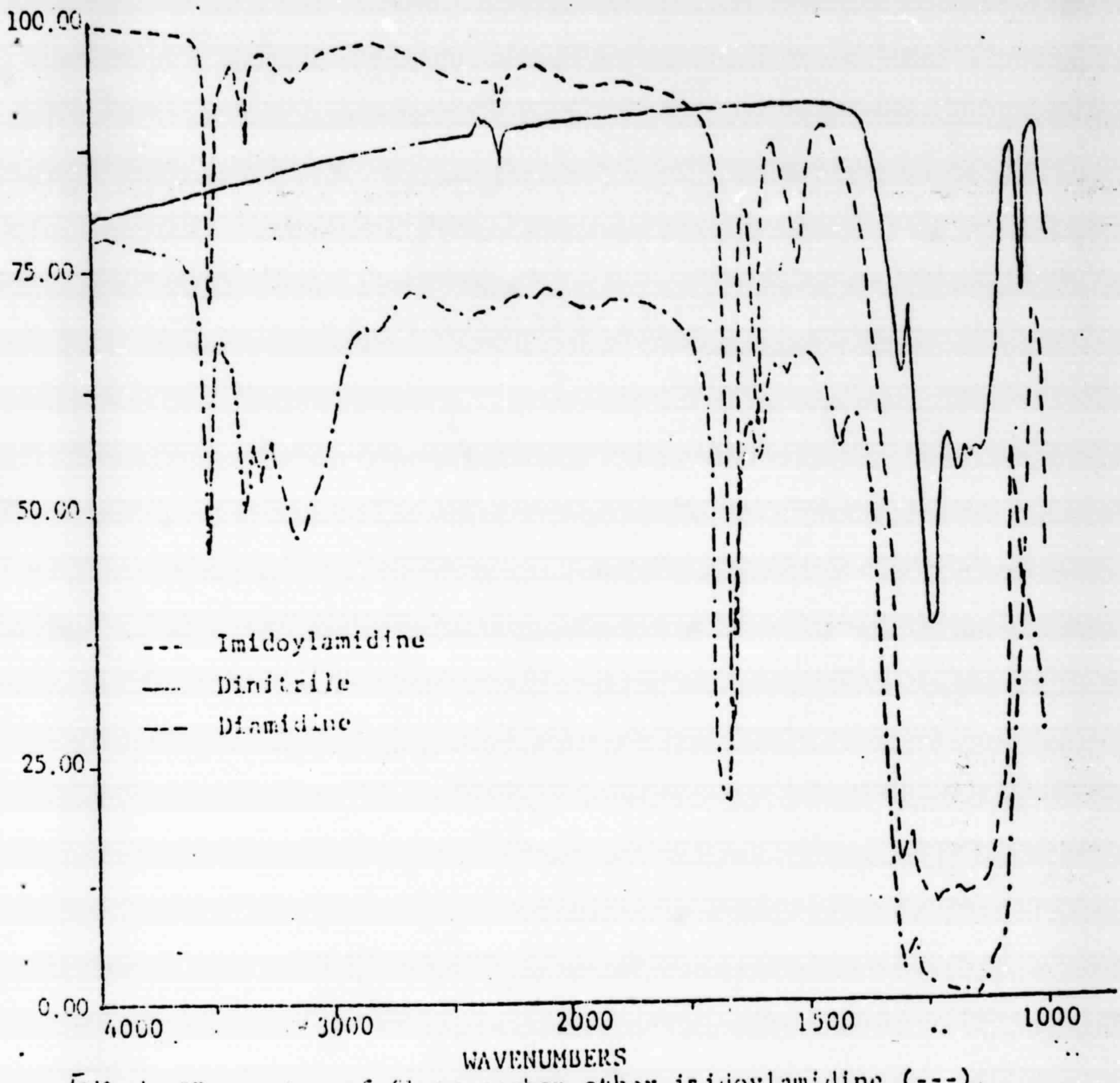


Fig. 1 IR spectra of fluorocarbon ether imidoylamidine (---), dinitrile (——), and diamidine (---)

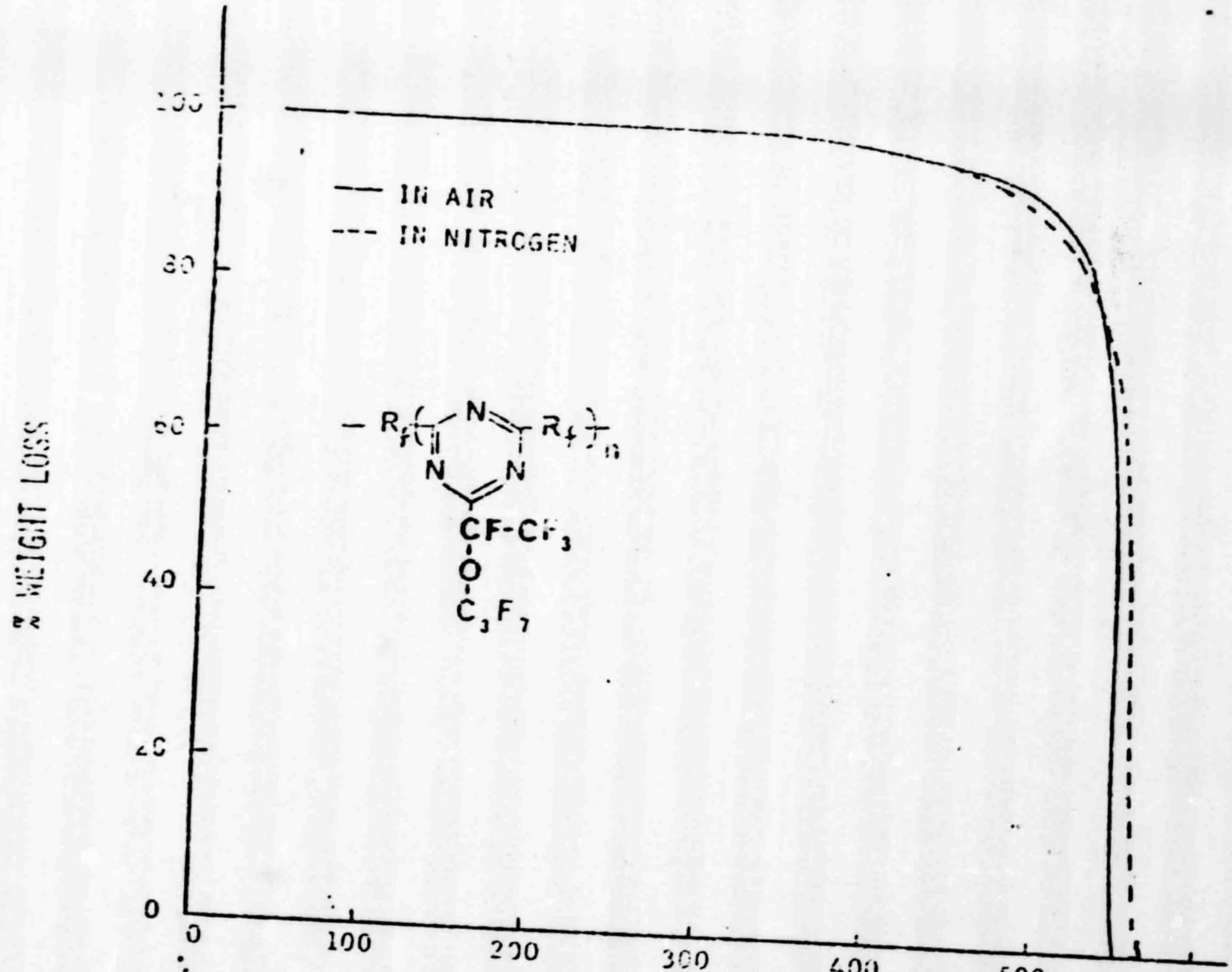


Fig. 2 THERMOGRAVIMETRIC ANALYSIS CURVES OF CURED FCE TRIAZINE ELASTOMER AT A HEATING RATE OF 10°C/MIN.

ORIGINAL PAGE IS
OF POOR QUALITY

Modification of Epoxy Reinforced Glass Cloth Composites with a Perfluorinated Alkyl Ether Elastomer

Synopsis

A perfluorinated alkyl ether diacyl fluoride prepolymer of high molecular weight was co-reacted with EPON 828 epoxy resin and diamino diphenyl sulfone to obtain an elastomer toughened glass cloth composite. Improvements in flexural toughness, impact resistance and water resistance without loss of strength, modulus or a lowering of the glass transition temperature were realized over that of the unmodified composite.

Introduction

Fiber reinforced epoxy composites have found widespread utility as structural materials. They have the advantage of having both high strength and high modulus to weight ratios, making them particularly useful in aeronautical and aerospace applications. The main drawback to these high modulus materials is their inherent brittleness which results in low impact strength.

Enhancement of the energy absorbing properties of thermoplastic and thermosetting resin systems depends not only on the degree of elastomer/resin compatability but also upon dispersing the rubber phase and controlling its particle size. In order to obtain a discreet rubber phase there must be a degree of incompatability between rubber and resin.[1] But, to insure efficient energy transfer, there must be molecular interaction between the two

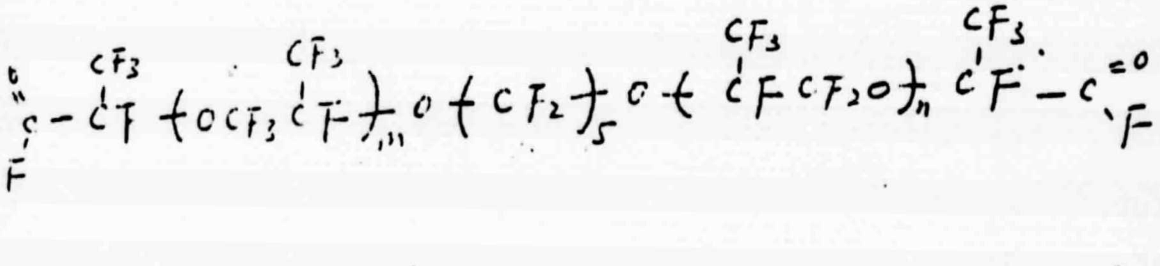
phases.[2] By controlling the amount of rubber added and the reaction conditions an empirical evaluation of the relationship of particle size to mechanical properties could be made, utilizing scanning electron microscopy.

In prior work, mostly in the CTBN (carboxylterminated butadiene-acrylonitrile copolymer) modification of epoxy resins, toughening has been realized with a concomitant loss of modulus (stiffness), and the ultimate use temperature of the plastic.[3] Ideally, one would like to improve toughness without compromising the other properties of epoxy resin systems that make them so useful. The work presented below concerns this problem by utilizing a high temperature, low modulus perfluorinated alkyl ether diacyl fluoride (EDAF) liquid prepolymer to modify an existing epoxy system. It will be demonstrated that this elastomeric prepolymer combines, to a certain degree, molecular incompatability and chemical interaction to obtain toughened epoxy/glass cloth composites with high modulus, strength and thermal stability.

Experimental

Formulation

Linear EDAF is a liquid prepolymer with pendant acyl fluoride functionality. It was obtained by PCR Research Chemicals, Inc. of Gainesville, Florida. The structure of EDAF can be represented as:



(where m+n = 5 to 6; reactive equivalence is 725 grams/equivalent)

4,4'-Diaminodiphenyl sulfone (DDS, 124 grams/equivalent) was used as the curing agent. DDS was obtained from Ciba-Geigy Corporation of Ardsley, New York under the trade name EPORAL. EPON 828, a diglycidyl ether of bisphenol A (DGEBA, 189 grams/equivalent, as determined by the pyridinium chloride method[4]) was purchased from the Shell Chemical Company.

EPON 828 was dissolved in enough acetone to obtain 50% solids in the final mixture. EDAF was then added and stirred for 15 minutes to pre-react with the epoxy. DDS was added and stirred until the solution became transparent. Stoichiometry was determined by starting with a control batch having 77% EPON 828 and 23% DDS by weight and adding varying amounts of EDAF by weight to make the modified samples. To maintain the reactive stoichiometry constant from sample to sample, equal equivalences of DDS were subtracted from the control formulation.

Preparation

Neat resin samples were prepared by taking the above formulations and pouring them into a high temperature RTV silicone dogbone mold. Using vacuum and heat the solvent was carefully removed before gelation. The temperature was raised gradually to 150°C for 1.5 hours to facilitate curing.

The fiber glass/resin composites were prepared by painting 12, 12 inch by 10 inch satin weave glass fiber sheets purchased from Uniglass Industries, style 01-01-7781, finish UM555 (an A-1100 amino silane sizing). Prepregs were made by staging at 80°C for 5 minutes and 120°C for variable times

depending on EDAF content. After lay-up, pressing was done at 150°C and 50 psi for 1.5 hours. The laminates were cooled at room temperature to avoid warping.

Infra-red Spectroscopy

The mixture obtained in the formulation was painted onto NaCl plates. The progress of the cure was observed by the disappearance of epoxy bands at $915cm^{-1}$ and $859cm^{-1}$, primary amine bands at $3410cm^{-1}$ and $3368cm^{-1}$, and the acyl fluoride band of EDAF at $1885cm^{-1}$. The reaction of epoxy and EDAF resulted in an ester linkage as demonstrated in the appearance of a carbonyl band at $1775cm^{-1}$.

Thermal Testing

The curing characteristics of the resin system were studied with a DuPont 901 Cell Base/990 Differential Scanning Calorimeter. Thermogravimetric analysis was done with a DuPont 951/990 Thermal Analyzer.

Morphology

The fracture surfaces obtained from tensile fracture of the neat resin dogbones were plated with Au/Pt and studied by scanning electron microscopy.

Typical electron micrographs are shown in Figure 1. Micrograph B shows a uniformly dispersed rubber phase in the brittle epoxy matrix.

Mechanical Testing

The neat resin dogbones were tensile tested according to ASTM designation D638-68, Standard Method of Test for the Tensile Properties of Plastics.

Test samples were cut from the fiber/epoxy laminates for dynamic mechanical analysis, 3 point flexural, tensile and short beam shear tests. Dynamic mechanical analysis was done on a DuPont 980 DMA, interfaced with a Digital MINC II instrument computer. The flexural, tensile and short beam shear tests were made with an INSTRON mechanical tester according to ASTM procedures D790-70, D638-68 and D2344-76 respectively. The short beam shear samples were impacted with a Gardner type ball impactor. Each value in Tables I and II represents the average of at least 6 samples.

Boiling Water Test

A control and an EDAF modifies dogbone sample were immersed in boiling water for 5 weeks and weighed at intervals to determine resistance water.

Results and Discussion

The impact of the amount of EDAF ~~elastomer~~ on the thermogravimetric, dynamic mechanical and tensile properties of the neat resin is shown in Table I. Study reveals that the addition of EDAF only slightly lowers the thermal stability while raising the position of the dampening peak in the temperature domain. The tensile properties improve dramatically at 3.0 % EDAF over that of the control and then drop off at higher concentrations. There appears to be an optimum of tensile reinforcement at the 2 to 4% EDAF level.

It was observed in the scanning electron micrographs that at low concentrations of EDAF (< 5%) there was no distinct rubber phase (see Figure 1B). As the percentage of EDAF was raised to 10% a very distinct rubber phase (seen as spheres in Figure 1C) was observed. Therefore, it seems that tensile reinforcement is optimum when no distinct rubber phase has been formed.

Table II documents the change of mechanical properties with a change in the amount of EDAF in the EPON/DDS/EDAF glass cloth composites. Obvious trends in toughening and strength are seen along with general improvement of the temperature position of the DMA dampening peak. Table III. Illustrates the impact resistance of the modified laminates in relation to that of the unmodified laminates. It is most interesting to note that flexural toughness and short beam shear properties after impact have been improved without compromising strength and modulus. In fact, there has been a significant increase in strength and modulus along with improvements in toughness.

The tensile properties of the composite show the same general trend of the neat resin dogbones. The flexural and short beam shear after impact proper-

ties show maximums in the 7 to 10% EDAF range. Drawing from the electron micrographs one could conclude that tensile properties are optimized when the extent of EDAF/EPON copolymerization results in a continuous matrix, where the EDAF/EPON copolymers are evenly distributed throughout the matrix. The inherent incompatibility of the fluorocarbon and the hydrocarbon has not resulted in phase separation due to the relatively low concentrations of the former. Compare Figures I and II. As one raises the concentration of the EDAF, regions of EDAF/EPON linear copolymers coalesce into spherical particles that become more distinct from the homopolymeric matrix. It is at this point that the flexural and impact resistant properties are greatest.

The improvement in dynamic mechanical properties are not easily explained morphologically. The dampening peak in the DMA experiment can be thought of as the glass transition temperature (Tg) of the composite and is indicative of the maximum use temperature of a material.[5] The addition of elastomers normally results in a lowering of the Tg. Chemically, it could be said that the highly electronegative fluorine atoms of the modifier afford a greater opportunity for hydrogen bonding. This would result in more intermolecular interaction and therefore, a stronger matrix. It would require more thermodynamic energy to overcome this bonding and an upward shift of the dampening peak in the temperature domain results.

Figure III. illustrates the weight gained by neat resin samples immersed in boiling water for 5 weeks. The EDAF modified sample shows a weight gain that is 39% lower than that of the unmodified control. It has been demonstrated that the introduction of long chain perfluoroalkyl modifiers gives epoxy

resins

of increased water resistance.[6] The hydrophobic nature of the fluorinated EDAF excludes water from the matrix.

Concluding Remarks

The wide spectrum of results from the various experiments demonstrates that the physical characteristics of the EDAF modified epoxy resin are complex. The increase in Tg indicates that on a chemical basis, an increase in crystallinity via hydrogen bonding (-H····F-) due to the addition of EDAF has overcome losses in Tg expected by the greater dampening effects of the elastomer. Strength, modulus and toughness, both flexural and tensile, increased. This indicates a situation where reinforcement has occured chemically (via a crosslinked, hydrogen bonded elastomer-epoxy copolymer/epoxy matrix) and physically (via a rubber phase/brittle polymer interface).

The physical significance of this is that morphologically there are regions of an elastomer-epoxy copolymer phase that is chemically linked with the brittle epoxy-diamine cured matrix. This system maximizes toughening through the mechanisms of rubber energy absorption, dilation (free volume) yielding, optimum rubber content, particle size, particle shape and interphase adhesion. All these can be incorporated into the craze/crack branching theory.[7] Perhaps this system can be more appropriately labeled as a Simultaneously Interpenetrating Polymer Network or SIN.[8] There exists a phase, where there is an SIN of the elastomer/epoxy copolymer within the epoxy/diamine copolymer. Here the rubber content is high and makes up the energy absorbing particles. There is then a gradual change or gradient that

sees the composition progress from the rubber like SIN into the brittle epoxy/diamine matrix. In this situation there is no abrupt interface. Adhesion between the rubber particles and the matrix is greatly enhanced and a more completely linked network is possible. Now, other properties, such as Tg, strength and modulus are not diluted by the addition of elastomer.

An SIN was produced by the simultaneous reaction of two independently crosslinking polymerizations in the same vessel. The actual dimensions of the dispersed rubber phase domains and the extent of molecular mixing between the components depended upon the relative polymerization rates or reaction gel times in relation to the time of phase separation. Further optimization of toughness was achieved by removing reaction conditions slightly from simultaneity (i.e. the actual reaction rate of the epoxy with EDAF is faster than that of the epoxy and the diamine).

ORIGINAL PAGE IS
OF POOR QUALITY

References

1. C.G. Bragaw, "The Theory of Rubber Toughening of Brittle Polymers," ACS Advances in Chemistry Series, "Multicomponent Polymer Systems," Vol. 176, p.100.
2. Ibid., p.91.
3. C.K. Riew, E.H. Rowe, H.R. Siebert, "Rubber Toughened Thermosets," ACS Advances in Chemistry Series, "Toughness and Brittleness of Plastics," Vol. 27, p. 330.
4. H. Lee, K. Neville, "Handbook of Epoxy Resins," McGraw-Hill, New York, 1967.
5. T. Murayama, "Dynamic Mechanical Analysis of Polymeric Material," Elsevier Scientific Publishing Company, New York, 1978.
6. J.R. Griffith, J.E. Quick, "Fluorine-Containing Epoxy Components and Plastics," ACS Advances in Chemistry Series, "Epoxy Resins," Vol. 2, p.15.
7. C.G. Bragaw, "The Theory of Rubber Toughening of Brittle Polymers," ACS Advances in Chemistry Series, "Multicomponent Polymer Systems," Vol. 176, p. 105.
8. R.E. Touhsaent, D.A.Thomas, L.H. Sperling, "Simultaneous Interpenetrating Networks Based on Epoxy/Acrylic Materials," ACS Advances in Chemistry Series, "Toughness and Brittleness of Plastics," Vol. 17.

Table I

Neat Resin Properties

Sample (% EDAF)	TGA 5% wt. loss (°C)	DMA T_g (°C)	Tensile Strength (psi x 10^3)	Tensile Modulus (psi x 10^5)
0	395	160	13.9	2.01
3	385	168	23.3	3.52
5	385	173	11.6	1.98
8	380	178	11.4	1.87

ORIGINAL PAGE IS
OF POOR QUALITY

Table II

Glass Cloth Composite Properties

Sample (% EDAF)	Flexural Strength (psi x 10^4)	Flexural Modulus (psi x 10^6)	Flexural Toughness (ft·lbs/in^3)	Tensile Strength (psi x 10^4)	Tensile Modulus (psi x 10^6)	Tensile Toughness (ft·lbs/in^3)	DMA Tg (°C)
0	5.78	3.10	36.5	4.46	2.26	77	203
3	8.04	3.72	51.8	5.65	2.63	103	216
5	9.02	4.36	52.4	5.07	2.57	83	212
8	9.55	4.32	60.4	4.85	2.31	76	225
10	7.06	3.27	41.0	4.07	2.14	62	206
20	2.75	1.98	11.5	2.20	1.92	19	190

Table III

Short Beam Shear - Impact Properties

Sample (% EDAF)	Short Beam Shear Strength (psi) No Impact	5 in·lbs Impact	% Loss
0	10,300	8,800	15
3	9,800	9,600	2
7	9,400	9,300	1
8	9,400	8,900	5
9	10,400	10,200	2
10	10,600	10,600	0

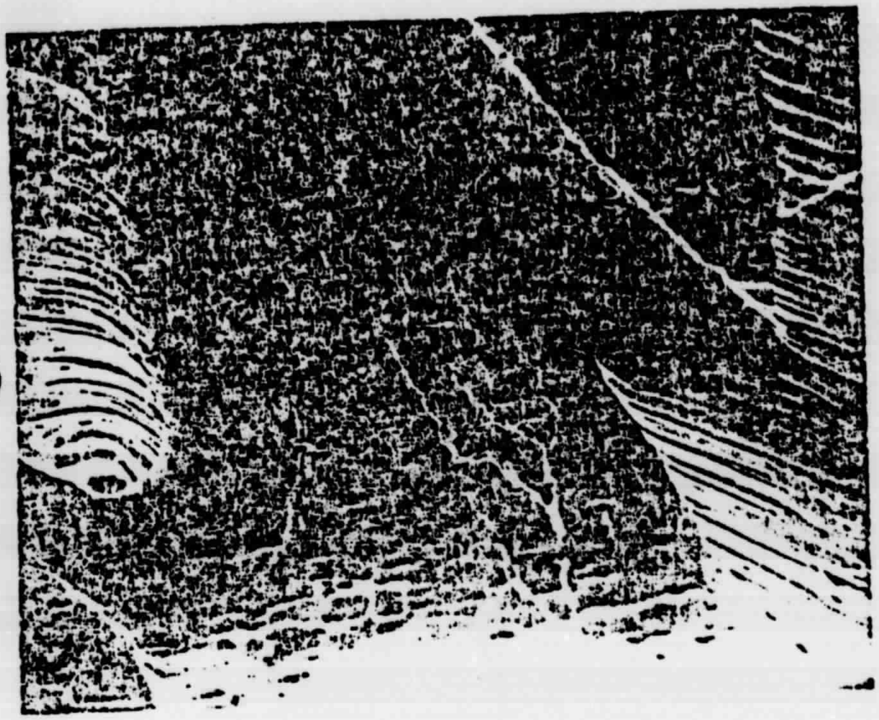


Figure 1. Electron micrograph of the fracture surface of neat resin containing 2% EDAF (2000X).

ORIGINAL PAGE IS
OF POOR QUALITY

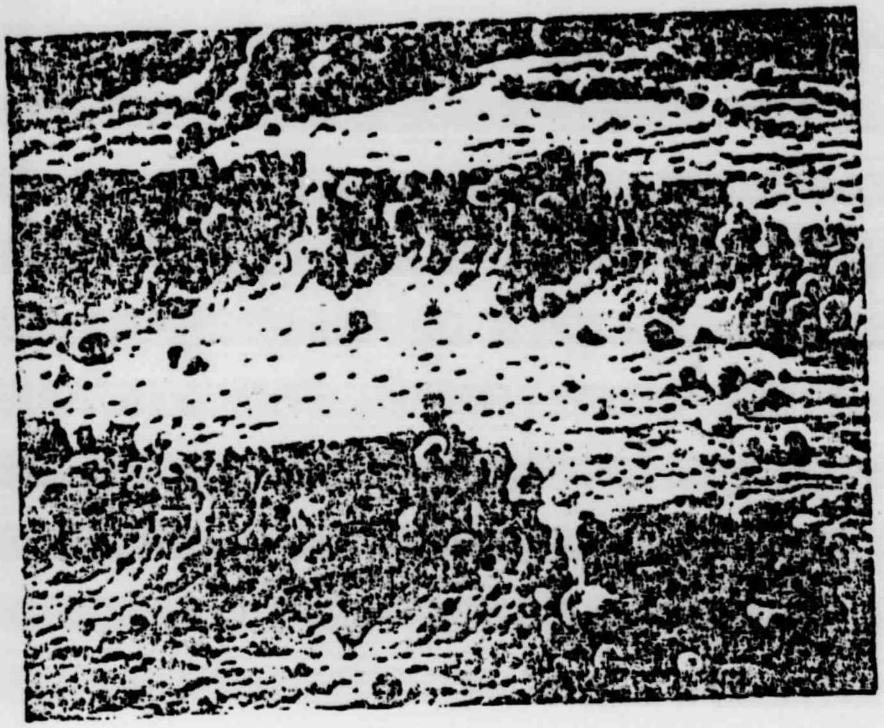


Figure 11. Electron micrograph of the fracture surface of neat resin containing 10% EDAF (300X).

Figure III.

Weight Gain in Boiling Water vs. Time
(% weight vs. weeks)